SHORT COMMUNICATIONS

Aluminum Chloride-Catalyzed Reactions of Organosilicon Compounds. A Rapid Redistribution Reaction of Chlorodisilanes

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In recent years, considerable attention has been directed toward a study of the organopolysilanes.[1] An interesting example of this involves the reaction of organodisilanes with an electrophilic reagent.[2] During the course of an investigation of the reactivity of organopolysilanes toward electrophiles, we have found that methylchlorodisilanes readily undergo aluminum chloride-catalyzed redistribution reaction at room temperature, while the disproportionation of alkylchlorosilanes catalyzed by aluminum chloride has been reported to proceed slowly, even at much higher temperatures.[3,4]

$$(CH_3)_3SiSi(CH_3)_3 + Cl(CH_3)_2SiSi(CH_3)_2Cl \xrightleftharpoons{AlCl_3} 2(CH_3)_3SiSi(CH_3)_2Cl \tag{1}$$

When an equimolar mixture of hexamethyldisilane and 1, 2-dichlorotetramethyldisilane is stirred at room temperature in the presence of anhydrous aluminum chloride (0.05—0.25 mol./l.), the equilibrium is established between pentamethylchlorodisilane and its original components within 1.5 hr.[5]

As the equilibrium is established rapidly in favor of pentamethylchlorodisilane, the reaction can be applied in a preparative scale. In a typical experiment a mixture of 73.5 g. of hexamethyldisilane, 94.5 g. of tetramethyldichlorodisilane, and 5.5 g. of anhydrous aluminum chloride was stirred for about 2 hr. at room temperature. After 3 g. of acetone had been added to the mixture to deactivate the catalyst, the mixture was subjected to simple distillation under reduced pressure. The fractionation of the distillate gave 114 g. (68.5%) of pure pentamethylchlorodisilane.

In view of these finidings, it became of interest to investigate the aromatic substitution by a mixture of pentamethylchlorodisilane and aluminum chloride, since it is well known that halosilanes do not react with benzene in the presence of Lewis acid.[3,4]

Although an attempted silylation of benzene by a mixture of pentamethylchlorodisilane and aluminum chloride was unsuccessful, we have found that detrimethylsilylation was effected very rapidly by pentamethylchlorodisilane in the presence of a catalytic amount of aluminum chloride.

$$\begin{aligned} &C_6H_5Si(CH_3)_3 + Cl\text{-}Si(CH_3)_2Si(CH_3)_3 \xrightarrow{AlCl_3} \\ &\qquad C_6H_5Si(CH_3)_2Si(CH_3)_3 + Cl\text{-}Si(CH_3)_3 \end{aligned} \tag{2}$$

Using competitive reaction conditions in benzene, we found that phenyltrimethylsilane underwent the reaction faster than *p*-chlorophenyltrimethylsilane and slower than *p*-methylphenyltrimethylsilane with pentamethylchlorodisilane.[6]

The order of substituent effects demonstrates the electrophilic nature of the reaction; it also confirms the present reaction to be a new class of aromatic electrophilic substitution.[7]

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[1] C. Eaborn, "Organosilicon Compounds," Butterworths Scientific Publications, London (1960), p. 351.

[2] H. Sakurai, T. Imoto, N. Hayashi and M. Kumada, *J. Am. Chem. Soc.*, **87**, 4001 (1965).

[3] H. Gilman and G. E. Dunn, *Chem. Revs.*, **52**, 77 (1953).

[4] G. A. Russell, *J. Am. Chem. Soc.*, **81**, 4831 (1959), and references therein.

[5] The apparent equilibrium constant, $K=[C_5H_{15}Si_2Cl]^2/[C_6H_{18}Si_2][C_4H_{12}Si_2Cl_2]$, was found to be 82.6 for the original mixture of 6.22 mmol. of hexamethyldisilane, 5.78 mmol. of tetramethyldichlorodisilane and 1 mmol. of aluminum chloride in 20 ml. of benzene. In chloroform, however, the reaction did not proceed even after one week at room temperature.

[6] The apparent relative rates at an early stage of the reaction were found: $k_{p\text{-}CH_3}/k_H=2.0$ and $k_{p\text{-}Cl}/k_H=0.2$.

[7] R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds," Elsevier Pubshing Co., Amsterdam (1965).